

**PATENT APPLICATION**

**IN THE UNITED STATES PATENT AND TRADEMARK OFFICE**

In re the Application of

Piotr KULA et al.

Group Art Unit: 1793

Application No.: 10/531,690

Examiner: W. ZHU

Filed: April 15, 2004

Docket No.: 122083

For: HYDROGEN GAS MIXTURE FOR THE UNDER-PRESSURE CARBURIZING  
OF STEEL

**DECLARATION UNDER 37 C.F.R. §1.132**

I, Piotr Kula, a citizen of Poland, hereby declare and state:

1. I have a degree in mechanical engineering, materials science and heat treating of metals which was conferred upon me by Politechnika Lodzka (Poland) in 1975.
2. I have been employed by Politechnika Lodzka since 1975 (since 1996 as professor), and I have had a total of 20 years experience in the field of steel carburizing.
3. I am a named inventor in the above-captioned patent application. I am familiar with the patent application.
4. I have a professional relationship with the Assignee, Seco/Warwick SP.ZO.O. and Politechnika Lodzka, of the above-identified patent application. In the course of that professional relationship, I received compensation directly from Seco/Warwick SP.ZO.O and Politechnika Lodzka for my work relating to research and development regarding steel carburization.
5. I and/or those under my direct supervision and control have conducted the following experiments in accordance with good laboratory practices.

6. The experiments use acetylene, ethylene and hydrogen at various compositions and proportions to carburize steel in a low pressure vacuum furnace chamber.

The experimental results demonstrate that the presently claimed acetylene/ethylene/hydrogen mixture for under-pressure carburizing steel achieves unexpected results in an intensive hydrocarbon decomposition along with an efficient carbon transfer at an acetylene to ethylene ratio of 0.55 when compared to Japanese Patent Publication No. 2000-001765 (hereinafter "JP 765") in which a gas mixture with a different ratio of acetylene to ethylene (only 0.428) is used to vacuum carburize steel.

#### **Experimental Conditions**

The charge containing low carbon steel sheets and three 17CrNi samples of total surface area of 0.4 m<sup>2</sup> were treated in the vacuum carburizing furnace. The furnace, experimental equipment and the investigated charge are illustrated below in Figures 1(a) to 1(d).

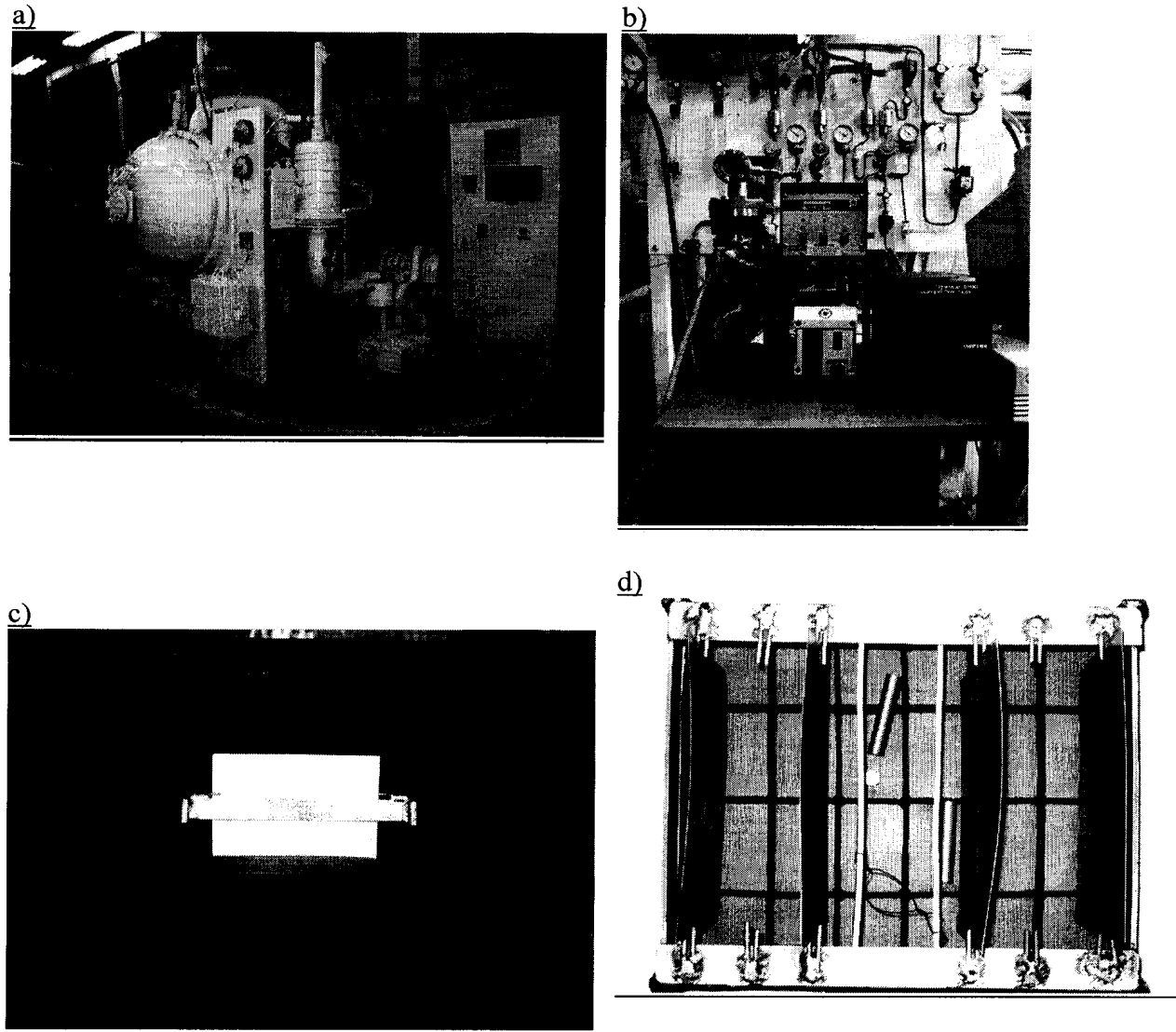


Figure. 1 Experimental equipment and charge arrangement: (a) vacuum carburizing furnace, (b) gas dosing system and mass spectrometer, (c) the charge in the furnace chamber and (d) the charge after process

Three different methods of gas dosing during the boost stage were tested in experimental tests and labeled as Experiment A, Experiment B and Experiment C. Each of the Experiments were conducted at the same (1) pressure (5 mbar), (2) boost time (10 minutes), (3) diffusion time (20 minutes), and (4) temperature (950°C).

Experiment A was conducted using a carbon carrier with an acetylene/ethylene ratio 0.55 (i.e., the lower end of the acetylene to ethylene ratio recited in claim 1) blended with hydrogen at a ratio of 1:1 carbon carrier (i.e., the total amount of acetylene and ethylene) to hydrogen. The volumetric flow rates of acetylene, ethylene and hydrogen in Experiment A were 33.6 L/hr, 61.4 L/hr and 95.0 L/hr, respectively.

Experiment B was conducted using a carbon carrier with an acetylene to ethylene ratio 0.428 (i.e., the ratio described in JP 765) blended with hydrogen at a ratio of carbon carrier to hydrogen of 1:1. The volumetric flow rates of acetylene, ethylene and hydrogen in Experiment B were 28.5 L/hr, 66.5 L/hr and 95.0 L/hr, respectively.

Experiment C was also conducted using a carbon carrier with an acetylene to ethylene ratio 0.428 (i.e., the ratio described in JP 765) blended with hydrogen. The volumetric flow rates of acetylene, ethylene and hydrogen in Experiment C were 26.3 L/hr, 61.4 L/hr and 95.0 L/hr, respectively. As such, the different amount of acetylene flow rates in Experiment A and Experiment C decreases the amount of carbon which can be transferred to the charge and further alters both the (1) acetylene to ethylene ratio (i.e., 0.428) and (2) carbon carrier to hydrogen ratio (0.92).

The parameters for Experiments A-C are illustrated below in Table 1.

Table 1: Parameters for Experiments A-C

Parameter	Experiment A	Experiment B	Experiment C
Acetylene (A) flow rate (L/hr.)	33.6	28.5	26.3
Ethylene (E) flow rate (L/hr.)	61.4	66.5	61.4
Hydrogen (H) flow rate (L/hr.)	95.0	95.0	95.0
Ratio A/E	0.55	0.428	0.428
Ratio (A+E)/H	1	1	0.92
Temperature (°C)	950	950	950
Time of boost (min)	20	20	20
Time of diffusion (min)	10	10	10
Pressure (mbar)	5	5	5
Charge (m <sup>2</sup> )	0.4	0.4	0.4

**Carbon Transfer Efficiency Evaluation**

The total amount of carbon in the carbon carrier that was introduced into the vacuum furnace chamber during Experiments A-C must have been transferred into one of three forms: (1) the charge, (2) the by-products (i.e., soot and/or tar) and (3) the exhaust gases. This relationship, derived from a mass balance around the vacuum furnace chamber, can be expressed by equation (1):

$$C_T = C_C + C_B + C_E \quad (1)$$

where  $C_T$  is the total amount of carbon introduced into the furnace chamber during carburization,  $C_C$  is the amount of carbon transferred to the charge during carburization,  $C_B$  is the amount of carbon transferred to the by-products (i.e., soot and/or tar) during carburization, and  $C_E$  is the amount of carbon in the exhaust gas that exits the vacuum furnace chamber.

By rearranging Equation 1, the amount of carbon transferred to the charge during carburization ( $C_C$ ) for Experiments A-C were evaluated using equation (2)

$$C_C = C_T - (C_B + C_E) \quad (2)$$

The  $C_B$  value for Experiments A-C was determined by using an EDS spectra and a SEM to measure the average thickness of soot and tar traces (1) on the charge and (2) on the furnace walls and equipment. The  $C_E$  value for Experiments A-C was determined by using a mass spectrometer to measure the carbon content in the exhaust gases.

Furthermore, the carbon transfer efficiency ( $C_{Eff}$ ) is determined by dividing the amount of carbon in the charge ( $C_C$ ) by the total amount of carbon provided ( $C_T$ ). Table 2 below summarizes the carbon transfer efficiency for Experiments A-C and the data used to determine the carbon transfer efficiency for Experiments A-C. Table 3 below summarizes the increase in the carbon transfer efficiency and the decrease in the amount of carbon in by-products (i.e., soot and tar) of Experiment A as compared to Experiment B and Experiment C.

Table 2: Summary of Carbon Transfer Efficiency Data and the Carbon Transfer Efficiency For Experiments A-C

Parameter	Experiment A	Experiment B	Experiment C
<b>Total Carbon (<math>C_T</math>)</b>	33.84 g	33.84 g	31.20 g
<b>Carbon In Exhaust (<math>C_E</math>)</b>	24.10 g	29.88 g	24.58 g
<b>Carbon in By-Products (<math>C_B</math>)</b>	0.65 g	1.70 g	0.93 g
<b>Carbon Transferred to Charge (<math>C_C</math>)</b>	9.09 g	2.26 g	5.69 g
<b>Carbon Transfer Efficiency (<math>C_{Eff}</math>)</b>	26.9 %	6.7 %	18.2 %

Table 3: Analysis of Case Depth for Experiments A-C

	<b>Increase in Carbon Transfer Efficiency</b>	<b>Decrease in Amount of Carbon By-Products</b>
<b>Experiment A Compared to Experiment B</b>	301.5 %	61.8 %
<b>Experiment A Compared to Experiment C</b>	47.8 %	30.1 %

As shown above in Table 2, the carbon transfer efficiency in Experiment A (0.55 acetylene to ethylene ratio) was approximately 26.9%, while the carbon transfer efficiency in Experiment B and C (0.428 acetylene to ethylene ratio) was 6.7% and 18.2%, respectively. Furthermore, as shown above in Table 3, Experiment A (1) increased the carbon transfer efficiency by 301.5% for Experiment B and over 47.8% for Experiment C and (2) decreased the amount of carbon by-products by 61.8% for Experiment B and by 30.1% for Experiment C.

Still further, the increase in carbon transfer efficiency was confirmed both quantitatively and qualitatively by metallographic investigations. The metallographic investigations consisted of using a SEM to measure the case depth (i.e., increased thickness) of the charge in Experiments A-C after carburization, which in turn, indicates the effectiveness of the carbon transfer close to the hole of the charge. Furthermore, the case depth is defined as the increased thickness of the charge as a result of the carburization, and was measured on (1) the outside of the hole, (2) the inside of the hole and (3) within the hole for each portion (i.e., the top portion and the bottom portion) of the hole for the charges produced in Experiments A-C.

The quantitative data for the case depth assessments of Experiments A-C are illustrated below in Table 4, and qualitatively illustrated below in Figures 2(a)-2(c). The

values listed below in Table 4 are the average values from three measurements for the top portion and the bottom portion of the hole for the charges produced in Experiments A-C. The evaluation of effective case depth was performed for the microstructure criterion 50% ferrite + 50% pearlite. Furthermore, the location of the case depth measurement site was selected close to the hole because this site exhibits a high sensitivity to the effectiveness of the carbon transfer from a gaseous phase to the surface of steel. However, the measurements obtained at this site are representative of the entire surface of the steel charge.

Table 4: Comparison of the Case Depth for Experiments A-C

Place of Measurement	Experiment A		Experiment B		Experiment C	
	Bottom Portion	Top Portion	Bottom Portion	Top Portion	Bottom Portion	Top Portion
Outside Of Hole	310 $\mu\text{m}$	312 $\mu\text{m}$	187 $\mu\text{m}$	212 $\mu\text{m}$	250 $\mu\text{m}$	275 $\mu\text{m}$
Within Hole	162 $\mu\text{m}$	168 $\mu\text{m}$	20 $\mu\text{m}$	32 $\mu\text{m}$	75 $\mu\text{m}$	100 $\mu\text{m}$
Inside Of Hole	-	100 $\mu\text{m}$	-	0 $\mu\text{m}$	-	45 $\mu\text{m}$



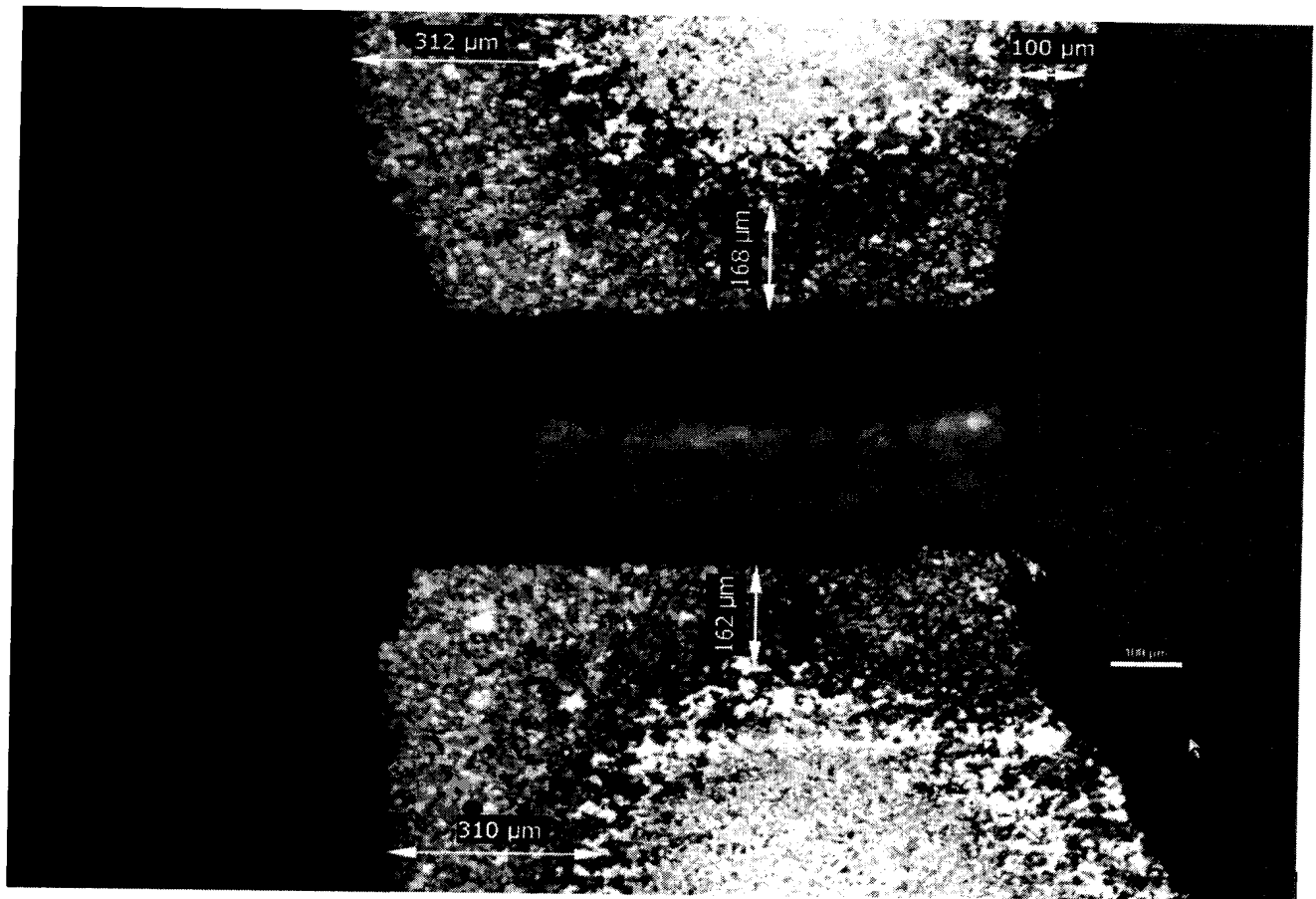


Figure 2(a). Metallography of Charge in Experiment A

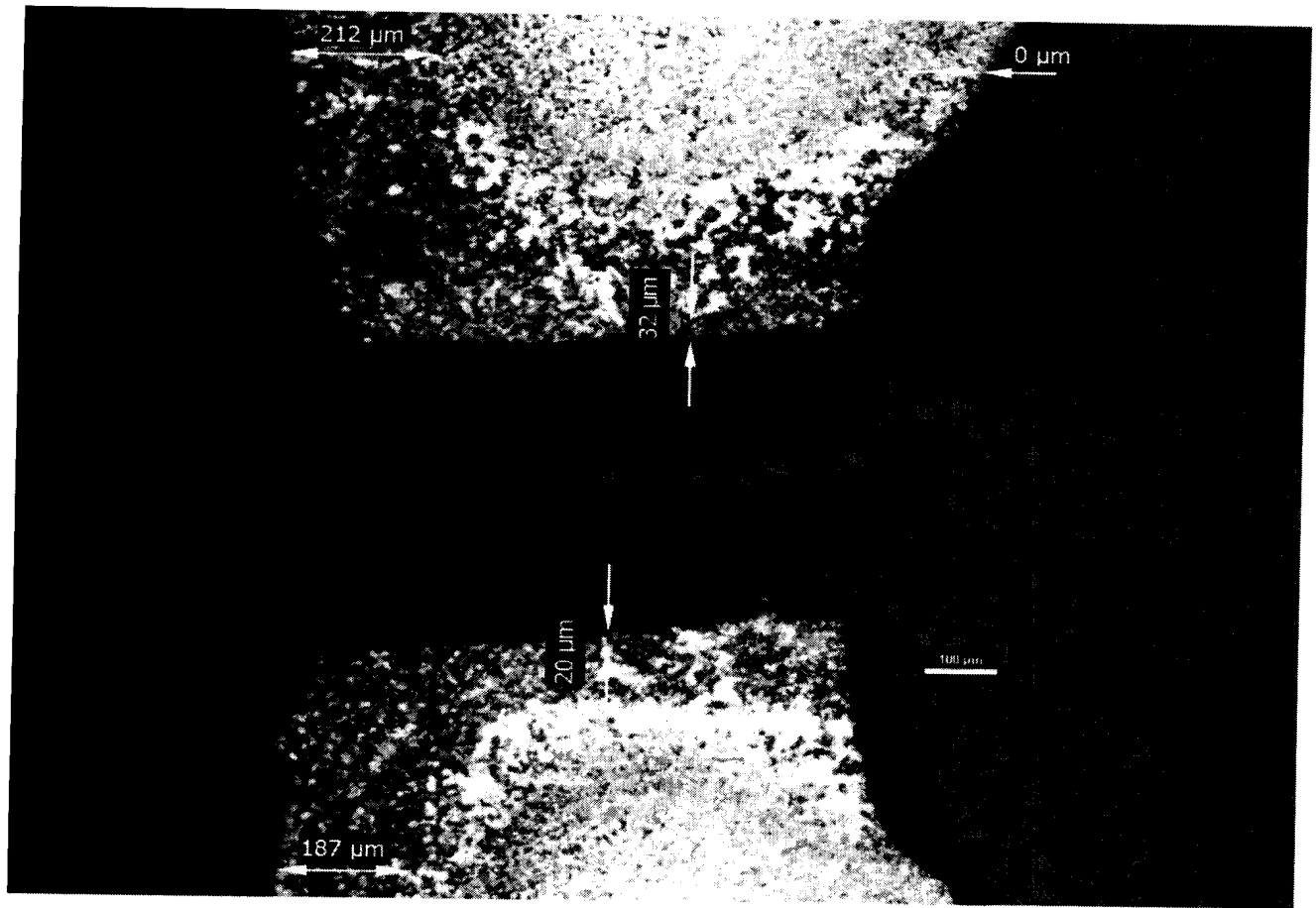


Figure 2(b). Metallography of Charge in Experiment B

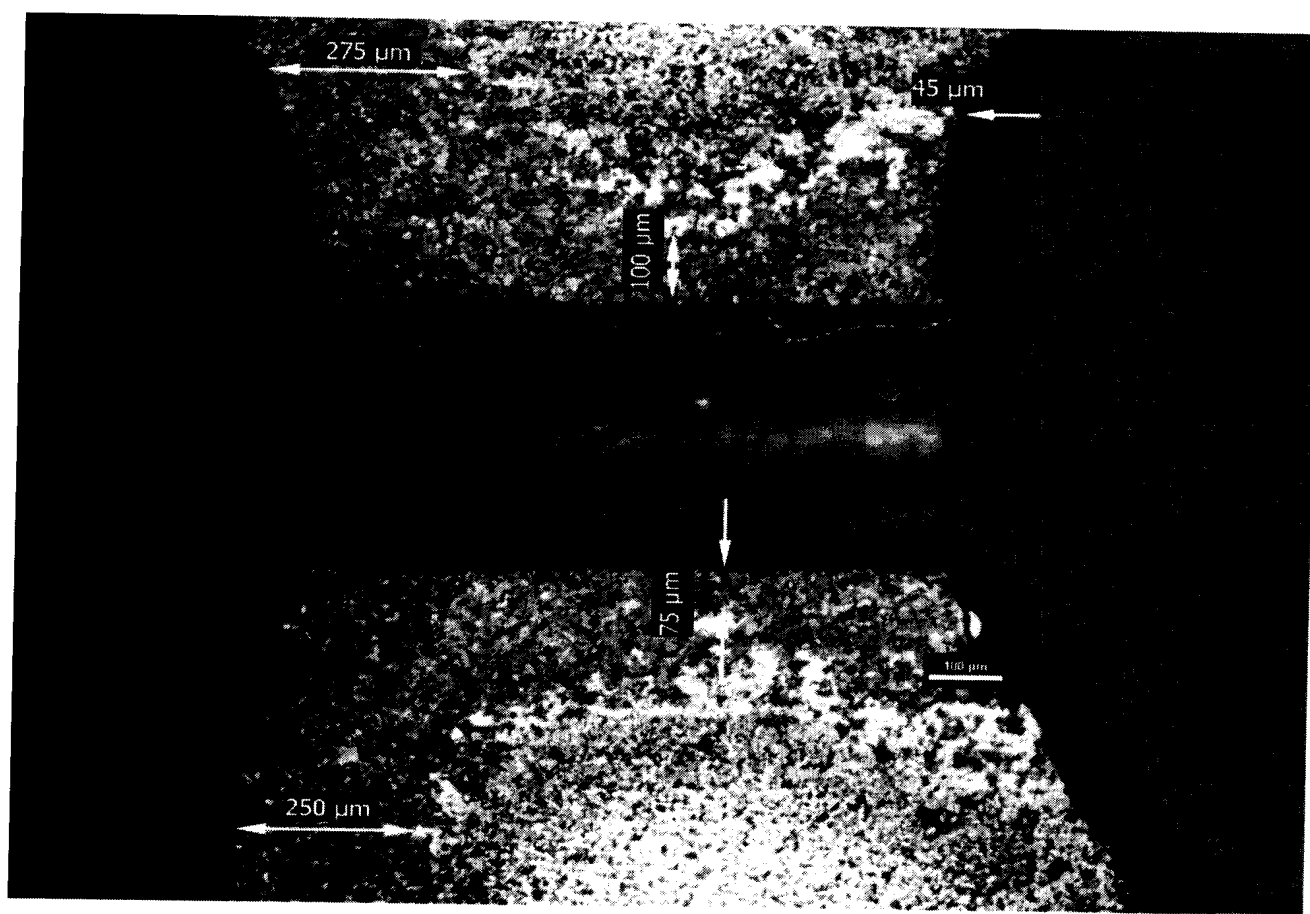


Figure 2(c). Metallography of Charge in Experiment C

Using the data in above Table 4, the percent increase in the case depth between Experiment A and Experiment B and the increase in case depth between Experiment A and Experiment C was calculated for both the top and bottom portion and is further summarized below in Table 5.

Table 5: Analysis of Case Depth for Experiments A-C

	Increase in Case Depth of Experiment A Compared to Experiment B		Increase in Case Depth of Experiment A Compared to Experiment C	
	Bottom Portion	Top Portion	Bottom Portion	Top Portion
Outside Of Hole	65.8 %	47.2 %	24.0 %	13.5 %
Within Hole	710.0 %	425.0 %	116.0 %	68.0 %
Inside Of Hole	-	undefined	-	122.2 %

As shown above in Table 5, the case depth for the charge for Experiment A (0.55 acetylene to ethylene ratio) increased by at least 47.2% when compared to the charge for Experiment B (0.428 acetylene to ethylene ratio). Furthermore, the case depth for the charge for Experiment A increased by at least 13.5% when compared to the charge for Experiment C (0.428 acetylene to ethylene ratio). As such, the above metallographic investigations further both qualitatively and quantitatively confirmed the improved carburizing ability of hydrocarbon gas mixture for an acetylene to ethylene ratio of 0.55 (the lower limit of the presently claimed range) in comparison to an acetylene to ethylene ratio 0.428 (disclosed in JP 765).

### **Conclusion**

As such, the experimental results demonstrate that the presently claimed hydrocarbon gas mixture for the under-pressure carburizing of steel achieves unexpectedly improved hydrocarbon (i.e., acetylene and ethylene) decomposition together with a more efficient carbon transfer from a gaseous phase to steel even at lower end of the acetylene to ethylene ratio recited in claim 1 (0.55) in comparison to an acetylene to ethylene ratio 0.428 (i.e., the ratio disclosed in JP 765).

Thus, the above results demonstrate that the acetylene to ethylene ratio of 0.55 to 2 is necessary to achieve a uniformly carburized layer with no accumulation of soot or tar. JP 765, with an acetylene/ethylene ratio outside of this range, does not achieve such results.

7. I hereby declare that all statements made herein of my own knowledge are true, and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine and/or imprisonment under Section 1001 of Title 18 of the United States Code, and that such willful false statements may jeopardize the validity of the application or any patent issuing therefrom.

Date: 7. 11. 2008

P. Kula  
Piotr Kula